ESTERIFICATION OF OLEIC ACID WITH ETHANOL CATALYSED BY 12-TUNGSTOPHOSPHORIC ACID SUPPORTED ON ALUMINA

CHE NORRIZUAN BIN CHE ABDUL RAHIM

Report submitted in fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

Ester of organic acids and alcohols form an industrially important class of substances. They are mainly produced as components of esterification reactions. Esterification as well as transesterification reactions has been largely applied to the production of biodiesel, which may be defined as alkyl esters of long chain fatty acids derived from renewable resources such as biomass. This work presents an impregnation route to support 12-Tungstophosporic Acid (H_3PW) on Alumina (Al_2O_3) in acidic aqueous solution (HCl 0.1 mol/L) at different ratios (5, 10, 15, 25, 40 and 60 wt%). The catalyst were further applied in the esterification of oleic acid with ethanol. The samples calcined at 200°C for 4 h were characterized by Fourier Transform Infrared Spectrosocy (FTIR), X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). The effect of the most relevant variables of the process such as ratio of catalyst (H_3PW/Al_2O_3) and reaction temperature was investigated in the present study. An optimum reaction performance , 80% of oleic acid conversion was achieved at 25 wt% catalyst loading, 60°C, 4 h reaction and 1:6 (oleic acid:ethanol) molar ratio. Studies show that the catalyst is feasible to be used for biodiesel production.

ABSTRAK

Ester asid organik dan alkohol membentuk kelas bahan-bahan perindustrian yang penting. Ia biasanya dihasilkan sebagai komponen tindak balas pengesteran. Pengesteran serta tindak balas "transesterification" sebahagian besarnya telah digunakan untuk pengeluaran biodiesel, yang boleh ditakrifkan sebagai alkil ester asid lemak yang berantai panjang yang diperolehi daripada sumber-sumber yang boleh diperbaharui seperti biojisim. Kerja ini membentangkan laluan penghamilan untuk menyokong 12-Tungstophosphoric Asid (H_3PW) ke atas Alumina (Al_2O_3) dalam larutan akueus berasid (HCl 0.1 mol/L) pada nisbah yang berlainan (5, 10, 15, 25, 40 dan 60% berat). Pemangkin terus digunakan dalam pengesteran asid oleik dengan etanol. Sampel yang "calcined" pada 200 °C selama 4 jam dicirikan oleh "*Fourier Transform Infrared Spectrosocy* (FTIR)", "*X-ray Diffraction* (XRD)" dan "*Thermogravimetric Analysis* (TGA)". Kesan pemboleh ubah yang paling relevan dalam proses seperti nisbah pemangkin (H_3PW/Al_2O_3) dan suhu tindak balas telah dikaji dalam kajian ini. Prestasi tindak balas yang optimum, 80% daripada penukaran asid oleik telah dicapai pada 25% berat pemangkin dimasukkan, 60 °C, 4 jam tindak balas dan 1:6 (asid oleik: etanol) nisbah molar. Kajian menunjukkan bahawa pemangkin layak digunakan bagi pengeluaran biodiesel.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
DEDICATION	iv
ACKNOWLEGDEMENTS	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	viii
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xv

CHAPTER 1 INTRODUCTION

1.1	Background of Study	1
1.2	Problem Statement	2
1.3	Research Objectives	3
1.4	Scope of Research	3
1.5	Significance of Study	4

CHAPTER 2 LITERATURE REVIEW

2.1	Biodiesel	5
2.2	Esterification	5
2.3	Catalyst	7
2.4	Homogeneous Catalyst	7
2.5	Heterogeneous Catalyst	9

CHAPTER 3 METHODOLOGY

3.1	Introduction	13
3.2	Material	15
3.3	Equipment/Apparatus	15
3.4	Preparation of xH_3PW/Al_2O_3	16
3.5	Characterization of Catalyst	17
	3.5.1 Thermogravimetric Analysis (TGA)	17
	3.5.2 Fourier Transform Infrared Spectrometer (FTIR)	17
	3.5.3 X-ray Diffraction (XRD)	17
3.6	Esterification Reaction	18
	3.6.1 Ratio of xH_3PW/Al_2O_3 where x is varied (5, 10, 15, 25, 40 and 60 wt%)	18
	3.6.2 Reaction temperature is varied from 55, 60, 70°C	19

3.7 Titration Process 19

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Introduction 21

4.2 Characterization of Aluminium Oxide Support 21

4.2.1 Thermogravimetric Analysis (TGA) 22

4.2.2 Fourier Transform Infrared Spectrometer (FTIR) 23

4.2.3 X-ray Diffraction (XRD) 25

4.3 Esterification Reaction of Oleic Acid with Ethanol 32

4.3.1 Effect of Catalyst Ration (xH_3PW/Al_2O_3) 32

4.3.2 Effect of Reaction Time for 25% H3PW/Al2O3 catalyst 34

4.3.3 Effect of Temperature for 25% H3PW/Al2O3 catalyst 36

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Introduction 38

5.2 Conclusion 39

5.3 Recommendation 40

REFERENCES		41
APPENDICES		43
A	Figure of Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectrometer (FTIR)	43
B	Figure of Equipment for Esterification Reaction	44
C	Figure of Equipment for Titration Process	47
D	Results from Characteristic of Catalyst (xH_3PW/Al_2O_3) by Thermogravimetric Analysis (TGA)	48
E	Results from Characteristic of Catalyst (xH_3PW/Al_2O_3) by Fourier Transform Infrared Spectrometer (FTIR)	50
F	Results from Characteristic of Catalyst (xH_3PW/Al_2O_3) by X-ray Diffraction (XRD)	53
G	Details Result from Esterification Reaction and Conversion Calculation	74
H	Details Calculation for Determine the Crystalline Size (TGA)	93

LIST OF TABLES

Table No.	Title	Page
2.1	Summary for the Homogeneous Catalyst	11
2.2	Summary for Heterogeneous Catalyst	12
3.1	Material and Function	15
3.2	Equipment and Function	18
4.1	Summary for XRD Analysis	31
4.2	Effect of Catalyst Ratio (xH_3PW/Al_2O_3)	32
4.3	Result for Effect of Reaction Time	34
4.4	Result for Effect of Temperature	36

LIST OF FIGURES

Figure No.	Title	Page
3.1	General Flow Diagram	14
4.1	Thermogravimetric curves for 12-tungstophosphoric acid supported on alumina catalyst (5 wt %)	22
4.2	FTIR analysis for Pure 12-tungstophophoric Acid	24
4.3	FTIR analyses for 5, 10, 15, 25, 40 and 60 wt% of catalyst	25
4.4	XRD Analysis for 5 % H_3PW/A_l2O_3	26
4.5	XRD Analysis for 10 % H_3PW/A_l2O_3	27
4.6	XRD Analysis for 10 % H_3PW/A_l2O_3	28
4.7	XRD Analysis for 25 % H_3PW/A_l2O_3	29
4.8	XRD Analysis for 40 % H_3PW/A_l2O_3	30
4.9	Graph Conversion (%) versus Catalyst Ratio (wt %)	33
4.10	Graph Conversion (%) versus Reaction Time (hr)	35
4.11	Graph Conversion (%) versus Temperature (ºC)	37

LIST OF SYMBOLS

%	Percentage
wt	Weight
°C	Degree celcius
h	Hour
w/w	Weight per weight
mol/L	Mol per litre
mL	Mililitre
mg	Miligram
°C/min	Degree celcius per minute
cm^{-1}	Centimeter power -1
°	Degree
α	Alpha
g/molg	Gram per mol gram
mL/min	Mililitre per minute
θ	Theta
cps	Centipose

LIST OF ABBREVIATIONS

PFAD	Palm Fatty Acid Distillate
FFA	Free Fatty Acid
FAME	Fatty Acid Methyl Ester
DMAP	Dimethylaminopyridine
PTSA	p-Toluenesulfonic Acid
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectrometer
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, biodiesel is very important to produce the energy source. Biodiesel can be used in any diesel engine when mixed with mineral diesel. The biodiesel industry in Malaysia is at a standstill stage with almost zero production. Many companies in Malaysia were not able to maintain their operations given the high cost of production and the lack of the much needed incentive and subsidies from the Government (U.R. Unnithan, 2010). The high cost of production can be price of oil increase in the world. This problem can be solving by new possible alternative such as biodiesel is on the rise around the world, due to a strong and growing desire.

Biodiesel fuel is the new possible alternative to replace the fossil fuel as the energy source such as in transportation sector. Esterification and transesterification is one of the methods to produce the fuel. Esterification of free fatty acid with alcohol can be produced the fuel. Usually the free fatty acids are found in vegetable oil and animal fats. Oleic acid is a monounsaturated of fatty acid and about 39.2% of oleic acid can be found in palm oil. If

free fatty acid higher in the palm oil, the production of biodiesel is lower. Then, the oil can be directly utilized in a transesterification reaction to reduce the free fatty acid in palm oil.

1.2 PROBLEM STATEMENT

Nowadays, whole world has faced a crisis in the crude oil price increase. The sudden crisis in the Middle East has made the world crude oil price increase. The sole depends to crude petroleum and diesel gives us no option left, which could contribute the sudden price increase in all industries.

The price of fossil fuels nowadays is increasing drastically that caused many other expenses to increase. Additionally, the dependencies on foreign countries can create negative impact on economy. With the price of fossil oil increasing each year due to the decreasing supply, it might be wise for Malaysia to adopt and implement the use of renewable fuel resources.

The major shift to Iceland usage of hydrogen in the public transportations an alternative to petroleum and diesel. The small country has gained respect to be the World´s Greenest Country thus set us example how we can actually swift from the traditional fuel to a new and environmentally safe energy.

In 2008 Malaysia gain the 26th spot in the World Greenest Country releases by the Yale EPI Statistic. The National Biofuel Policy that has been launched in that year was seen as a move by many to help our country to reduce environmental pollution. But the implementation of the key point of that respective policy has yet too fat from realization. The result is significant. In the latest ranking released last year, Malaysia drop to 54th rank.

Some of the industry used the homogeneous catalyst in their process or reaction. Homogeneous catalyst usually not environmental friendly, a large amount of waste, corrosive and difficult of being sorted out makes part of the reaction product work up. No homogeneous catalyst yet for cracking process, reformation and ammonia synthesis.

1.3 RESEARCH OBJECTIVE

1.3.1 To develop of supported 12-Tungstophosphoric Acid on Aluminium Oxide catalyst for the esterification of Oleic Acid with Ethanol.

1.3.2 To characterize the developed catalyst

1.3.3 To determine the optimum operating condition of the esterification reaction with Oleic Acid and Ethanol with supported 12-Tungstophosporic Acid.

1.4 SCOPE OF RESEARCH

The scopes of this research are listed as below:-

i. Ratio of xH_3PW/Al_2O_3 where x is varied (5, 10, 15, 25, 40 and 60wt%).

ii. Thermogravimetric Analysis, Fourier Transform Infrared Spectroscopy and X-ray Diffraction will be used to determine the characteristics of catalyst.

iii. The reaction temperature will be varied from 55, 60 and 70°C.

1.5 SIGNIFICANCE OF STUDY

The research will develop catalyst for biodiesel production. The research also to contribute to the reduction of gasoline usage by boosting efficiency of green technology such as biodiesel, bioethanol and biobutanol. The road transport network accounts for 22% of all greenhouse gas emissions and through the use of biodiesel using agriculture raw material some of these emissions will be reduced as the fuel crops absorb the carbon dioxide. The research also used solid catalyst to reduce waste production of biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 BIODIESEL

Biodiesel is non-petroleum-based diesel produce by composed of long-chain free fatty acid with alcohol. Biodiesel produced by the reaction of a vegetable oil with ethyl or methyl alcohol by presence of catalyst. In chemically, biodiesel is called ethyl ester if the ethanol is use for alcohol (T.C.Shean Yaw et al., 2008).

Methyl and ethyl esters of fatty acids (biodiesel) are nontoxic, biodegradable and excellent replacement for petroleum (diesel) (H. Noureddini et all., 2004).

2.2 ESTERIFICATION

Esterification is a chemical process that the reaction between alcohols and carboxylic acids for production of esters. It also looks briefly at making esters from the reactions between acyl chlorides (acid chlorides) and alcohols, and also reactions between acid anhydrides and alcohols (Jim Clark, 2003). The reaction of an alcohol with an acid chloride (R-CO-Cl) or an anhydride (R-CO-O-COR') produce ester product (R-CO-OR') is

the union of the acyl group (R-C=O-) from the acid, RCO-OH, with the alkoxide group (R'O-) from the alcohol , R'-OH rather than other possible networking.

Chongkhong et al., (2007) studied the production of biodiesel by esterification of palm fatty acid distillate. The palm fatty acid distillate (PFAD) having high free fatty acids (FFA). The scope of study the influence of reaction temperature of 70-100°C, molar ratio of methanol to PFAD of 0.4:1–12:1, quantity of catalyst of 0-5.502% (wt of sulfuric acid/wt of PFAD) and the reaction times of 15-240 min. In their findings, it was observed that optimum conversion was achieved at the molar ratio of 4.3:1. The molar ratio is increasing did not significantly increase the amount of Fatty Acid Methyl Ester (FAME). The rapid formation of FAME was observed within the first 90 min. After 90 min, the conversion rate of FAME was slowly and steady state at the end reaction. Temperature from 70 to 100°C for all molar ratios, the FAME content was increased but the conversion rates were reduced at temperature 90-100°C. The maximum amount of FAME when use 1.834 wt% of H_2SO_4 acid catalyst in the reaction. When increase the amount of catalyst higher than 1.834 wt%, there was no enhancement of FAME content.

Sakthivel et al., (2008) studied an efficient catalyst for the esterification of long-chain fatty acids and alcohols in supercritical carbon dioxide by MCM-48 supported tungstophosphoric acid. The esterification is done by using alcohol and long-chain fatty acids. In their findings, the catalytic activities in *sc*-CO_2 medium were significantly higher than as in mesitylene medium. By loading on MCM-48, HPW gave higher activity for the esterification. With the increase in chain length of acid and alcohols in the esterification in *sc*-CO_2, the yields of esters was increased. The HPW catalyst particularly appropriate useful for the esterification of fatty acids with primary fatty alcohols but the relatively very low yields in the esterification including some short acid and alcohols, secondary alcohols and functional acids. The esterification of long-chain fatty acids and alcohols in sc-CO_2 medium very actively with HPW and MCM-48 supported HPW catalysts.

2.3 CATALYST

Catalyst is a substance for change in rate of a chemical reaction. A catalyst may participate in multiple chemical transformations. Promoter is a substance that increasing the reactivity of catalyst while catalytic poisons is a substance that deactivated catalyst. Catalyst divided by heterogeneous catalyst and homogeneous catalyst. Heterogeneous catalysts such as Palladium on activate charcoal used in the reaction of hydrogen with nitro groups to produce amine groups. Homogeneous catalyst such as DMAP (dimethylaminopyridine) used in solution to catalyst esterification reactions.

2.4 HOMOGENEOUS CATALYST

Vicente et al., (2003) studied a comparison of different homogeneous catalyst system (Integrated biodiesel production). A comparison is made of different basic catalyst which is sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide for methanolysis of sunflower oil. In their findings, the methyl ester concentrations were near 100wt% when used four catalysts. For the methoxide catalysts, biodiesel yields were higher than 98wt% after the separation and purification step while biodiesel yields for sodium and potassium hydroxide were lower namely 85.9 and 91.67 wt%. The biodiesel yields can be higher when a modification of the value for experimental conditions such as temperature and catalyst concentration.

Aranda et al., (2007) studied the acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. In this experiment, used different of homogeneous catalyst such as sulfuric acid, methanesulfonic acid, phosphoric acids were the best catalysts. In their findings, sulfuric and methanesulforic acids were the best catalyst, with conversion higher than 90% at 1 h of reaction for reactant methanol and ethanol. For different alcohols, methanol reaction was faster than ethanol. For effect of

water in the reaction medium, inhibition effect can be found in the ethanol reaction. A small amount of catalyst (0.01 w/w) is enough to promote the reaction.

Joseph et al., (2005) studied a green, efficient and reusable catalyst system and reaction medium for Fischer esterification by bronsted acidic ionic liquids. Bronsted acidic ionic liquid containing nitrogen based organic cation 1-methylimidazole and 1-buthyl-3-methylimidazolium and inorganic anions of the type BF4, PF6 and PTSA. In their findings, a maximum 100% conversion and 100% product selectivity was obtained on using PTSA as catalyst over a period of 2 h. For PF6 used in the reaction also gave 100% conversion in 2 h but only 90% selectivity for ester was achieved. In the effect of mole ratio of imidazole and BF4 that on increasing the amount of anion in the ionic liquid, the conversion increases but the selectivity remains the same. The reaction had to be carried out for longer time for complete conversion. When the temperature was increase to 120°C, the conversions also increase.

Tosh et al., (2000) studied the homogeneous esterification of cellulose in the lithium chloride-N, N-dimethylacetamide solvent system: effect of temperature and catalyst. In their findings, LiCL-DMAc was found to be an excellent solvent system for the acetylation of cellulose with acetid=c anhydride in the presence of p-TsCL or pyridine. Pyridine is more active as a catalyst for esterification than p-TsCL. In case of esterification with higher anhydrides, p-TsCL might serve as a better catalyst.

Di Serio et al., (2005) studied the synthesis of biodiesel via homogeneous lewis acid catalyst. In their finding, bivalent cations are catalyst for both transesterification and esterification reactions. Catalytic activities are related to the lewis acid strength of the metals and to the molecular structure of the anion a complex. The best catalytic performances were obtained with cation metals having stability constant with

dibenzoilmetane in the range between 8.60 (corresponding to cadium) and 10.23 (corresponding to zinc). Then, the stearates have better performances than acetates.

2.5 HETEROGENEOUS CATALYST

Heterogeneous catalyst was present in a different phase, usually in solid phase. Heterogeneous catalyst has many advantages that main advantage is the relative ease of catalyst separation from the product stream that aids in the creation of continuous chemical processes. Heterogeneous catalyst was typically more tolerance of extreme operation condition. It is to be select for this experiment.

Marchetti et al., (2006) studied the heterogeneous esterification of oil with high amount of free fatty acids. In their experiment, basic resin was use as a heterogeneous catalyst. In their findings, the final conversion follows an endothermic behavior when temperature is changes. Resin should be added during the process at initial FFA amounts changes to increase the final conversion. On the amount catalyst, when more catalyst is added a little higher reaction rate is achieved. In the resin is reused, the final conversion is achieved for 2nd, 3rd, and 4th reuse was less than 25%. They conclude that the resin should to be regenerated after each process and resins are a heterogeneous catalyst is appropriate to perform the esterification with higher conversion.

Joo Kim et al., (2004) studied the transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. In their experiment, Na/NaOH/γ-Al_2O_3 is use for heterogeneous base catalyst. In their finding, the activities of the heterogenous base catalysts correlated with their basic strengths. *n*-hexane was the most effective with a loading amount of 5:1 VO to *n*-hexane molar ratio when the co-solvent tested. The ratio optimum methanol to oil loading was found to be 9:1. For different catalyst, the

Na/NaOH/γ-Al_2O_3 heterogeneous base catalyst showed almost the same activity under optimized reaction condition compared to the homogeneous NaOH catalyst.

Sejidov et al., (2005) studied the esterification reaction using solid heterogenous acid catalyst under solvent-less condition. In their finding, esterification reaction of phthalic anhydride by 2-ethylexanol in the presence of solid acidic catalyst have been investigated under solvent-less condition. For the best reactivity and efficiency among the investigated heterogenous catalyst is sulfated zirconia. These catalysts are environmentally friendly and cleaner than homogeneous catalyst.

Moo Park et al., (2008) studied the heterogenous catalyst system for the continuous conversion of free fatty acid in used vegetable oils for the production of biodiesel. In their finding, the SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be effective in the esterification of free fatty acid to FAME. When the properties of the catalyst are different, it is difficult to compare batch reaction with packed-bed reactions. Packed-bed reactions have advantages over batch reactions in terms of mass production but have some disadvantages when their activity is considered. For maximize the activity of the catalyst, the optimization of the catalyst pellet size will be needed. For the characterization, the oxidation state of W is mainly related to the catalytic activity of WO_3/ZrO_2.

Table 2.1: Summary for the Homogeneous Catalyst

Author	Reaction	Catalyst	Finding
Vicente et al., (2003)	Esterification (Biodiesel production from sunflower oil)	Sodium Methoxide, Potassium Methoxide, Sodium Hydroxide and Potassium Hydroxide	Biodisel yields were higher when used Methoxide catalyst.
Aranda et al., (2007)	Esterification (Biodiesel production from Palm Fatty Acid)	Sulfuric Acid, Methanesulfonic Acid, phosphoric Acid and Trichloroacetic Acid	Sulfuric and Methanesulfonic Acids were the best catalyst.
Joseph et al., (2005)	Esterification (Acetic acid with Benzyl Alcohol)	Bronsted Acidic ionic liquid (BF4, PF6 and PTSA)	PTSA is the best catalyst than BF4 and PF6.
Tosh et al., (2000)	Esterification (Cellulose in the lithium chloride–*N*,*N*-dimethylacetamide solvent system)	*p*-TsCL and Pyridine	Pyridine is more active as a catalyst for esterification than *p*-TsCL.
Di Serio et al., (2005)	Transesterification and Esterification (Triglycerides (TG) with Methanol)	Lewis Acid catalyst	The best catalytic performances were obtained with cation metals having stability constant.

Table2.2: Summary for Heterogeneous Catalyst

Author	Reaction	Catalyst	Finding
Marchetti et al., (2006)	Esterification (Oil with high amount of free fatty acids)	Basic resin	The basic resin is the best catalyst for esterification reaction.
Joo Kim et al., (2004)	Transesterification (Vegetable oil to biodiesel using heterogenous base catalyst)	$Na/NaOH/\gamma\text{-}Al_2O_3$	$Na/NaOH/\gamma\text{-}Al_2O_3$ heterogenous base catalyst showed almost the same activity.
Sejidov et al., (2005)	Esterification (Phthalic Anhydride by 2-Ethylhexanol)	Sulfated Zirconia	Sulfated Zirconia is the best reactivity and efficiency.
Moo Park et al., (2008)	Esterification (Oleic Acid with Methanol)	SO_4/ZrO_2 and WO_3/ZrO_2	The SO_4/ZrO_2 and WO_3/ZrO_2 catalysts were found to be affective in the esterification of free fatty acid to FAME

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

The steps involved in order to obtain experiment of results are catalyst preparation analyze of each of the catalyst involve in order to determine the it's characteristic and perform the activity studies. The general flow of the experiment is illustrated in the figure 3.1.